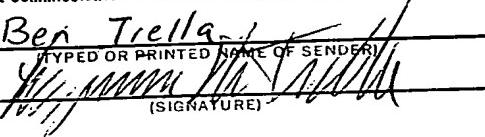


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ZERO VOLATILE ORGANIC COMPOUND COMPOSITIONS BASED UPON
ORGANIC SOLVENTS WHICH ARE NEGLIGIBLY REACTIVE WITH
HYDROXYL RADICAL AND DO NOT CONTRIBUTE APPRECIABLY TO
THE FORMATION OF GROUND BASED OZONE

Cross-Noting to Related Applications

This application claims the benefit of U.S. Provisional Application No. 60/053,073, filed July 18, 1997.

Background of the Invention

5 This invention pertains to the art of solvent blends and solvent/resin blends. More, particularly this invention pertains to blends that do not contribute to the formation of ground based ozone or smog. The invention is particularly applicable to solvent blends and
10 solvent/resin blends that have no volatile organic compounds for use with adhesives, coatings, inks, cleaning and blowing agents and the like and will be described with particular reference thereto. However, it will be appreciated that the invention may be advantageously
15 employed in other environments and applications.

Heretofore, hydrocarbon-based solvents have been used to dissolve organic materials in many industrial applications. However, recently, hydrocarbon-based solvents have fallen out of favor because they have been
20 classified by the United States Environmental Protection Agency and other international regulatory bodies as materials that contribute to the formation of ground based ozone or smog. This has created a need for other types of solvents for the production of coatings, adhesives, inks and the like.
25

Upon evaporation, a highly-reactive, hydrocarbon-based solvent reacts with hydroxyl radicals and ultraviolet light very close to the ground to form a photochemical smog that is considered harmful and in some

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cases dangerous. Some cities have severe smog which reduces visibility and actually causes "ozone alerts". In part, the smog is caused by hydrocarbon emissions from cars. However, another major contributor is industrial use of hydrocarbon-based solvents such as hexane and toluene.

The benchmark for desired reaction rates of hydrocarbon-based compounds is ethane. If a compound has a reaction rate with the hydroxyl radical and ultraviolet ("UV") light that is faster than ethane, the compound reacts too close to the ground and consequently generates ozone and smog. Such compounds are defined as volatile organic compounds (VOCs). On the other hand, if a compound has a reaction rate that is slower than ethane, the compound reaches higher into the atmosphere before reacting with the hydroxyl radical and UV light. In such instances the non-VOC compound does not contribute to the formation of ground based ozone and smog.

Some of the more reactive VOCs are:

toluene;
methyl ethyl ketone;
diacetone alcohol;
hexane;
isopropyl alcohol;
pentane;
dibasic esters;
trichloroethylene;
benzene;
ethyl acetate;
butyl acetate;
n-methyl pyrrolidone;
glycol ethers;
d-limonene;
terpene hydrocarbon solvents;
dimethyl ether; and,
tetrahydrofuran.

Governmental regulations limit the use of VOCs in coatings, inks, and adhesives. As a result, water-borne coatings have become the most important type of coatings in coating and adhesive systems. However, water-borne coatings must contain some volatile organic compound content. This is because water flashes off too fast from the water-based latex or emulsion to make a good film. To alleviate this problem, 7-10% of a slower evaporating solvent such as a glycol ether is added to the latex to aid in film formation. Unfortunately, glycol ethers are primary examples of VOCs and thus dangerous to the environment.

Halogenated hydrocarbon-based compounds have reaction rates that are slower than ethane. However, these halogenated compounds are ozone depleting. consequently, they are not suitable VOC-free solvents.

In the prior art, United States Patent No. 5,102,563 to Desbiendras describes a solvent composition which contains methyl tert butyl ether. However, methyl tert butyl ether is a VOC and thus unsafe for the environment. Similarly, Patent No. 4,898,893 to Ashida describes a composition for making a blowing agent which contains a flammable aliphatic hydrocarbon. This is also a VOC. Patent No. 3,950,185 to Toyama teaches film removing compositions which contain methylene chloride and bromochloromethane which are not VOCs. However, these compositions also contain methanol and monochlorobenzene which are VOCs. Patent No. 3,924, 455 to Begishagen describes a formulation containing mineral spirits which removes lacquer stress coatings. These mineral spirits are also VOCs.

An object of the present invention is the identification of some high-performance solvents and solvent/resin blends which are non-flammable or self-extinguishing and do not contribute to the formation of ground-based ozone.

Another object of the present invention are solvents and solvent/resin blends that are safer to the environment than even water-based systems which still must contain a volatile organic solvent to aid in film formation.

Yet another object of the present invention are environmentally-safer solvent compositions which do not contribute to the formation of ground based ozone which will be useful in the formulation of cleaning agents, coatings, adhesives, inks and also blowing agents for the production of plastic foams.

Summary of the Invention

The present invention contemplates new and improved solvent and solvent-resin compositions which overcome all of the above referenced problems and others and which are economical and effective for their intended uses.

In accordance with the present invention, there is provided a solvent-resin composition having generally zero volatile organic compounds (VOCs). The composition consists essentially of a resin component and a solvent component. The solvent component is 5-95% by total volume of the solvent-resin composition and is one or more of the zero-VOC solvents selected from the group consisting of:

chlorobromomethane;
1-bromopropane;
n-alkane (C₁₂-C₁₈);
t-butyl acetate;
perchloroethylene;
benzotrifluoride;
parachlorobenzotrifluoride;
acetone;
1,2-dichloro-1,1,2-trifluoroethane;
dimethoxymethane;

1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxybutane;

2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;

5 1-ethoxy-1,1,2,2,3,3,4,4-nonafluorobutane; and,

2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane.

In accordance with a more limited aspect of the
10 invention, the solvent component is present in the amount
40-95% by total volume of the composition.

In accordance with a still more limited aspect
of the invention, the solvent component is present in the
amount 30%-80% by total volume of the composition.

15 A principal advantage of the invention is that
it is environmentally safer yet still capable of
effectively dissolving resins.

20 Another advantage of the invention is that it
may be used in place of solvents currently used for inks,
adhesives, coatings and the like.

Still other advantages and benefits of the
invention will become apparent to those skilled in the art
upon a reading and understanding of the following detailed
description.

25 Detailed Description of the Preferred Embodiments

The compositions of the present invention are
high-performance solvent and solvent-resin blends that are
generally free of VOCs. The compositions as herein
described and as set forth in the claims are expressed in
30 terms of percentages by volume unless clearly indicated to
the contrary.

In describing the compositions of the present
invention, reference will be made to certain resin
classifications which require a totally VOC-free solvent
35 system to be environmentally safe. These resin
classifications are:

- a) acrylic-thermoplastic;
- b) acrylic-thermosetting;
- c) chlorinated rubber;
- d) epoxy (either one or two part);
- 5 e) hydrocarbon (e.g., olefins, terpene resins, rosin esters, coumarone-indene, styrene-butadiene, styrene, methyl-styrene, vinyl-toluene, nitrocellulose, polychloroprene, polyamide, polyvinyl chloride and isobutylene);
- f) phenolic;
- 10 g) polyester and alkyd;
- h) polyurethane;
- i) silicone;
- 15 j) urea; and,
- k) vinyl and vinyl acetate.

It is to be appreciated that this list does not include all resin classifications. Other resin classifications 20 are intended to be encompassed by the scope of the present invention.

Effective solvents of the present invention which have reaction rates with hydroxyl ion slower than ethane are:

- 25 1) chlorobromomethane;
- 2) 1-bromopropane;
- 3) methyl acetate;
- 4) n-alkane (C₁₂-C₁₈);
- 5) t-butyl acetate;
- 30 6) perchloroethylene;
- 7) benzotrifluoride;
- 8) parachlorobenzotrifluoride.
- 9) acetone;
- 10) 1,2-dichloro-1,1,2-trifluoroethane
- 35 11) dimethoxymethane;

- 12) 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane;
- 13) 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;
- 5 14) 1-ethoxy-1,1,2,2,3,3,4,4-nonafluorobutane;
- 15) 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane;
- 16) methylene chloride; and,
- 10 17) technical white oils (mineral oils).

It is to be appreciated that this list does not include all effective non-VOC solvents. Other effective non-VOC solvents are intended to be encompassed by the scope of the present invention.

15 The type of specific applications (hence the denotation "a" alongside the number identifying the application) for which the solvents and solvent-resin blends of the present invention may be used are as follows:

- 20 1a) adhesives
2a) blowing agents
3a) coatings
4a) cleaning compositions
5a) inks

25 The zero-VOC solvent and solvent-resin blends of the present invention as well as their applications are set forth in the table below. The table uses the identifiers set out above, i.e., a numeral alone for the solvent and a numeral followed by "a" for the application.

30 SOLVENT AND SOLVENT-RESIN COMPOSITIONS HAVING ZERO VOCs

T90X

<u>MAIN COMPONENT</u>	<u>HOW USED</u> (blends are 5-95% or, more preferably, 40-95% by vol.)	<u>RESINS THAT FORM A FILM AFTER SOLVENT EVAPORATES</u>	<u>APPLICATIONS</u>
chlorobromomethane	by itself or blended with any of solvents 2-16 to obtain desired properties	a-k	1a-5a
1-bromopropane	by itself or blended with solvents 1, 3-16	a-k	1a, 3a, 5a
methyl acetate	blended with solvents 1,2, 4-16 at 10-95% by volume.	a-d, styrene, g, j, k	1a-5a
n-alkane (C12-C18)	by itself or blended with solvents 1-3,5-16	e	1a, 3a, 4a, 5a
t-butyl acetate	by itself or blended with solvents 1,4,6-16	a-d, styrene, g, j, k	1a, 3a, 4a, 5a
perchloroethylene	1-5,7-16	a-k	1a,3a,4a,5a
benzotrifluoride	1-6, 8-16	a-k	1a,3a,4a,5a
parachlorobenzotri fluoride	1-7, 9-16	a-k	1a,3a,4a,5a
acetone	1-5,7-16	a, b, e-h, k	1a-5a

	1,2-dichloro- 1,1,2- trifluoroethane	1-9, 11-16	a, k	1a-5a
	dimethoxymethane	1-3, 7-10, 12-16	a	1a-5a
5	1,1,1,2,2,3,3,4,4- nonafluoro-4- methoxy-butane	1-11, 13,15	a	2a, 4a
10	2- (difluoromethoxy- thyl)- 1,1,1,2,3,3,3- heptafluoropropane	1-12, 14,15	a	2a, 4a
15	1-ethoxy- 1,1,2,2,3,3,4,4,4- nonafluorobutane	1-13, 15	a	2a,4a
20	2- (ethoxydifluoromet hyl)- 1,1,1,2,3,3,3- heptafluoropropane	1-4	a	2a,4a
	methylene chloride	2-15	a-k	1a-5a
	technical white oils (mineral)	1-16	a,e,g	5a

25 A better understanding of the present invention
can be had by reference to the following descriptions of
embodiments which effectively meet the objectives outlined
above.

One preferred embodiment includes mixing one or
more of the polymeric resins:

30 acrylic-thermoplastic;
 acrylic-thermosetting;
 chlorinated rubber;
 epoxy resin;

hydrocarbon (e.g., olefins, terpene resins,
rosin esters, coumarone-indene, styrene-
butadiene, styrene, methyl-styrene, vinyl-
toluene, nitrocelullose, polychloroprene,
5 polyamide, polyvinyl chloride and
isobutylene);

phenolic;

polyester and/or alkyd;

polyurethane;

silicone;

urea; and/or

vinyl or vinyl acetate,

with 10-90%, by total volume of the composition, of one or
more of non-VOC solvents such as:

15 chlorobromomethane;

1-bromopropane;

methyl acetate;

n-alkane (C₁₂-C₁₈);

t-butyl acetate;

20 perchloroethylene;

benzotrifluoride;

parachlorobenzotrifluoride;

acetone;

1,2-dichloro-1,1,2-trifluoroethane;

25 dimethoxymethane; and/or

methylene chloride.

The individual solvents or blends thereof are added until
all of the resin(s) is dissolved.

In an embodiment for coatings and/or adhesives,
30 the mixture preferably has a high resin content, i.e., a
resin content of 20%-60% by volume. In another embodiment
for inks, the mixture preferably contains a lower
concentration of the resin, i.e., 5%-30% by volume. In
yet another embodiment, various pigments or additives are
35 added to achieve a desired range of properties.

In another preferred embodiment of the present
invention, 5-90% methyl acetate, by total volume of the

composition, is added to 10-95% of a solvent or solvent blend selected from the group:

chlorobromomethane;

1-bromopropane;

n-alkane (C₁₂-C₁₈);

t-butyl Acetate;

perchloroethylene;

benzotrifluoride;

parachlorobenzotrifluoride;

acetone;

1,2-dichloro-1,1,2-trifluoroethane;

dimethoxymethane;

1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-

butane;

2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;

1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane; and,

2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane.

These formulations are used as a cleaning composition for the removal of hydrocarbon or ionic contaminates from circuit boards or in the formulation of coatings, inks, or adhesives. Of course, the formulations may be used for other applications as well.

The following enumerated embodiments have the ability to dissolve resins for the production of coatings, adhesives, and inks as well. In addition, the embodiments are equally useful as cleaning formulations. The ranges for the embodiments are expressed in % by volume of the total solvent-resin composition or, alternatively, the total solvent composition of an initially non-resin containing solvent, such as a cleaning composition. The embodiments are:

- (1) 10-90% benzotrifluoride and 10-90% of one or more of the solvents:

- (a) 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxybutane;
- (b) 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;
- 5 (c) 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane;
- (d) 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane;
- (e) perchloroethylene;
- 10 (f) 1-bromopropane;
- (g) acetone;
- (h) n-alkane (C₁₂-C₁₆);
- (i) t-buyl acetate (C₁₂-C₁₆); and,
- (j) parachlorobenzotrifluoride;
- 15 (2) 5-20% benzotrifluoride and 80-95% 1-bromopropane;
- (3) 10-90% acetone and 10-90% n-alkane (C₁₂-C₁₈);
- (4) 10-90% 1-bromopropane and 10-90% of one or more of:
- 20 (a) chlorobromomethane; and,
- (b) n-alkane (C₁₂-C₁₈);
- (5) 10-90% parachlorobenzotrifluoride and 10-90% of one or more of:
- (a) 1-bromopropane;
- 25 (b) chlorobromomethane;
- (c) t-butyl acetate; and,
- (d) n-alkane (C₁₂-C₁₈);
- (6) 10-90% 1,2-dichloro-1,1,1-trifluoroethane and 10-90% of one or more of:
- 30 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxybutane;
- 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;
- 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane;
- and,
- 35 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane;
- 1-bromopropane

acetone;
benzotrifluoride; and,
methyl acetate.

Analogously, the following VOC-free embodiment
5 has the ability to dissolve resins for the production of
coatings, adhesives, and inks as well. In addition, the
embodiment is equally useful in cleaning formulations:

10-90% methylene chloride and 10-90% of one or
more of the following solvents:

10 chlorobromomethane;
1-bromopropane;
methyl acetate;
n-alkane (C₁₂-C₁₈);
t-butyl acetate;
15 perchloroethylene;
benzotrifluoride;
parachlorobenzotrifluoride;
acetone;
1,2-dichloro-1,1,2-trifluoroethane; and,
20 dimethoxymethane.

An added benefit to mixing methylene chloride with other
solvents is the reduction in the overall toxicity of
methylene chloride.

Other preferred solvent-resin compositions
25 include VOC-free solvents which have the ability to
dissolve resins for the production of coatings, adhesives,
and inks. The compositions include any of the above-
listed resins and the following solvent mixtures, which
are expressed in terms of % by volume of the solvent-resin
30 composition:

- (1) 1-20% technical white oil and 10-90% n-alkane
(C₁₂-C₁₈);
- (2) 1-20% technical white oil and 10-90% methyl
acetate;
- 35 (3) 1-20% technical white oil and 10-90% t-butyl
acetate;

- (4) 1-20% technical white oil and 10-90% benzotrifluoride;
- (5) 1-20% technical white oil and 10-90% acetone;
- (6) 1-20% technical white oil and 10-90% 5 parachlorobenzotrifluoride;
- (7) 1-20% technical white oil and 10-90% parachlorobenzotrifluoride;
- (8) 1-20% technical white oil and 10-90% perchloroethylene;
- 10 (9) 1-20% technical white oil and 10-90% methylene chloride; and,
- (10) 1-20% technical white oil and 10-90% of a mixture of methylene chloride, acetone, t-butyl acetate, methyl acetate and perchloroethylene.

15 The following VOC-free embodiment, expressed in terms of % by volume of total composition, is useful as an environmentally-safer blowing agent composition for the production of polyurethane or isocyanurate foams:

20 99-99.98% 1,2-dichloro-1,1,1-trifluoroethane and 0.01-0.5% alpha-methyl styrene to inhibit polymerization. In addition this embodiment has the ability to dissolve resins for the production of coatings, adhesives, and inks, and is useful in cleaning formulations.

25 Another embodiment useful as an environmentally-safer blowing agent composition is:

100 parts by weight polyether triol;
50 parts by weight toluene diisocyanate or toluene disocyanurate;

30 2 parts by weight water;
0.15 parts catalyst;
0.5-2 parts surfactant; and,
4-10 parts 1-bromopropane or chlorobromomethane.

Still another embodiment useful as an 35 environmentally-safer blowing agent composition, in terms of percent by weight of the total composition (including catalyst and surfactant), is:

50-70% polyether triol;
20-40% toluene diisocyanate or toluene
disocyanurate;

0-10% water;

5 0-5% catalyst;

0-5% surfactant;

2-15% 1-bromopropane or chlorobromomethane. The appropriate catalysts and surfactants are selected from those known in the art.

10 A more limited embodiment useful as an environmentally-safer blowing agent composition, in terms of percent by weight of the total composition (including catalyst and surfactant), is:

60-65% polyether triol;

15 30-33% toluene diisocyanate or toluene disocyanurate;

1-2% water;

0.09-2% catalyst;

0.3-1.5% surfactant; and,

20 2.4-6.1% 1-bromopropane or chlorobromomethane.

This composition is useful for the manufacture of a flexible furniture grade foam with a density of 0.024 g/cm³. blowing agent.

An embodiment of a zero-VOC adhesive is 25 350 grams of 1-bromopropane and/or benzotriflouride to which is added 30-50% by weight of a hydrocarbon resin, preferably an olefin, rosin ester or terpene resin, which acts as a tackifier. Then, 100 grams of styrene-butadiene polymer, polychloroprene polymer, polyvinyl chloride polymer, acrylic, epoxy, urethane, nitrocellulose, or styrene is added to the mixture. This mixture produces a contact adhesive with excellent bond strength. Another preferred embodiment of this mixture contains approximately 40-90%, volume, of 1-bromopropane and/or benzotriflouride, 5-35% of a hydrocarbon resin, and 5-25% 30 of styrene-butadiene polymer, polychloroprene polymer,

polyvinyl chloride polymer, acrylic, epoxy, urethane, nitrocellulose, or styrene.

Another zero-VOC adhesive starts with 100 grams of 1-bromopropane and/or benzotrifluoride. Then, 10-100 grams of styrene-butadiene, polychloroprene, polyvinyl chloride, acrylic, epoxy, urethane, nitrocellulose, or styrene polymer or resin is added. This also produces a contact adhesive with excellent bond strength. It is appreciated that other additives may be used to improve wetting and defoaming although they are not always required. Another preferred embodiment of this mixture contains approximately 40-95%, by volume, of 1-bromopropane and/or benzotriflouride, and 5-60% of styrene-butadiene, polychloroprene, polyvinyl chloride, acrylic, epoxy, urethane, nitrocellulose, or styrene polymer or resin. Still another preferred embodiment of this mixture contains approximately 70-95%, by volume, of 1-bromopropane and/or benzotriflouride, and 5-30% of styrene-butadiene, polychloroprene, polyvinyl chloride, acrylic, epoxy, urethane, nitrocellulose, or styrene polymer or resin.

Still another embodiment of a zero-VOC adhesive starts with 350g 1-bromopropane and/or benzotriflouride. Then, 20-100 grams of styrene butadiene rubber is added. Optionally, 5-10%, by volume, acetone is added to improve solubility if necessary. Another preferred embodiment of this mixture contains approximately 50-90%, by volume, of 1-bromopropane, and 10-30% of acrylic polymer or urethane polymer. Optionally, 5-10%, by volume, acetone is added to improve solubility if necessary.

The following VOC-free embodiment has the ability to dissolve resins for the production of coatings, adhesives, and inks as well. Further, the solvent includes stabilizers to stabilize against attack on aluminum. In addition, the embodiment is useful in cleaning formulations:

70-90%, by volume, 1,2-dichloro-1,1,1-trifluoroethane; 9-29% dimethoxymethane; and 0.5% butylene oxide and 0.5% nitromethane to 5 stabilize against attack on aluminum. Optionally, 5-10%, by volume, acetone is added to the total composition to improve solubility if necessary.

All of the embodiments of the present invention may interchangeably use any of the other non-VOC solvents 10 listed above.

The invention has been described with reference to the preferred embodiments. Obviously, modifications and alterations will occur to others upon a reading and understanding of this specification. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.